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(54) Title: PROCESS FOR SEPARATING LIQUID MIXTURES

(57) Abstract: A process for the separation of a liquid mixture using a ZIF. The liquid mixture can comprise - water, - one or more gases, - water and alcohol



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PROCESS FOR SEPARATING LIQUID MIXTURES

The present invention provides a process for separating liquid mixtures.

The separation of mixtures of compounds is a common process in the chemical industry. Separation processes are used for separating a wide range of compounds. Examples of mixtures that may need to be separated include for instance aqueous solutions of alcohols, mixtures of water and hydrocarbons, e.g. alkanes or higher alcohols, and mixtures of hydrocarbons, e.g. alcohol/alcohol, alcohol/alkane or alkane/alkane.

Conventionally, such mixtures are separated by distillation. However, distillation processes are energy consuming and cannot always economically produce high purity compounds. For instance, in the case of the separation of ethanol and water, the maximum ethanol purity which can be achieved economically is 95% ethanol. The existence of an azeotrope of the ethanol/water mixture prevents obtaining a purity above 96% ethanol without taking specific extra measures.

In addition, in case of dilute mixtures, i.e. relative low amounts of ethanol in water, large amounts of water need to be removed. It would be beneficial to remove the ethanol rather than to concentrate the mixture by removing water.

Other processes for separating such mixtures include membrane-based separations. In US 20070031954, a process for producing and recovering light alcohols from for instance fermentations broths is disclosed. In US 2007003195, a dilute mixture of ethanol and water comprising up to 20 wt% of ethanol is separated using a

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pervaporation membrane separation processes. The obtained permeate comprised in between 15 and 70 wt% of ethanol. In order to increase the ethanol content in the permeate, the permeate is subsequently subjected to a dephlegmation and second membrane separation process.

The membrane process of US 20070031954 cannot produce a high purity ethanol permeate without requiring subsequent purification of the permeate. There is a need in the art for a separation process, which can separate dilute mixtures efficiently.

In M.T.Holtzapple, R.F. Brown, Conceptual design for a process to recover volatile solutes from aqueous solutions using silicalite, Sep. Technol., vol 4, 1994, p213, a process for removing various alcohols from diluted aqueous alcohol solutions is described. In Holtzapple, a hydrophobic silicalite zeolite is used to concentrate an 1 wt% aqueous solution is contacted with the zeolite to separate the alcohol from the solution. The obtained alcohol product still comprised 76, 66 and 50 wt% water for starting solutions of 1 wt% ethanol, 1-propanol, and 1-butanol, respectively.

It has now been found that liquid mixtures can be separated using a zeolitic imidazolate framework material(ZIF).

Accordingly, the present invention provides a process for the separation of liquid mixtures using a ZIF.

It will be understood that separation herein does not per se refer to a complete separation into the pure components of the mixture, but rather to a process wherein one or more compounds present in the mixture are preferentially absorbed in the ZIF and isolated from the

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mixture in a concentrated form compared to the original mixture.

Reference herein to a ZIF is to a material comprising, essentially consisting of or consisting of zeolitic imidazolate framework. Preparation and characterisation of ZIFs have been extensively described in the literature, for instance by Yaghi et al. (Yaghi et.al, Proceedings of the National Academy of Sciences, volume 103, no. 27, 2006, p10186-10191, Yaghi et al, Nature materials, volume 6, July, 2007, p501-505 and Yaghi et al., Science, volume 319, no. 5865, 2008, p939-943). At least 35 ZIFs, including ZIF termed ZIF-1 to -12 and -20 to -23, have been synthesized as crystals by copolymerization of either Zn(II) (ZIF-1 to -4, -6 to -8, and -10 to -11) or Co(II) (ZIF-9 and -12) with imidazolate-type links, new ZIF types include structures wherein one or more of the carbon atoms of a benzimidazolate linker have been replaced by nitrogen atoms, giving ZIF-20 and -21 (purinate linker), ZIF-22 (5-azabenzimidazolate linker) and ZIF 23 (4-azabenzimidazolate linker). These ZIF materials are disclosed in detail in WO2007/101241, which is hereby incorporated by reference. The ZIF crystal structures are based on the topologies of seven distinct aluminosilicate zeolites: tetrahedral Si or Al atoms and the bridging O atoms are replaced with transition metal ions and imidazolate linkers, respectively. It will be appreciated by the skilled person that a ZIF is not a zeolite, on the contrary they are materials belong to the Metallic Organic Framework family of materials.

ZIFs are typically hydrophobic and they are stable in water, alkaline environments and organic solvents. The ZIFs have a high porosity and good thermal stability,

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e.g. characterisation of ZIF-8 and -11 has demonstrated a permanent porosity (Langmuir surface area: ZIF-8= 1,947 m²/g, ZIF-11= 1,676 m²/g) and a thermal stability up to 550°C.

5 The ZIFs have a high internal volume, typically in the range of from 0.5 to 1.6 ml/g ZIF. For comparison, typical zeolites have a upper inner volume limit of approximately 0.3 ml/g zeolite.

10 The present process provides an efficient separation process whereby specific compounds in a liquid mixture are preferentially absorbed by the ZIF, allowing selective removal of such compounds from the liquid mixture. Reference herein to absorbed is to both the absorption and adsorption of material. Depending on the
15 compound to be removed, the compound may be adsorbed on the surface of a ZIF or partially or completely absorbed into the internal volume of the ZIF crystal structure.

20 The ZIFs are very hydrophobic, therefore it is not generally necessary to perform any pre-drying or dehydration steps to remove residual water prior to use.

25 Due to the above-mentioned hydrophobic nature of the ZIFs, they are especially suitable for separating aqueous liquid mixtures, whereby the water uptake of the ZIF is minimal.

30 As mentioned herein above, the process according to the invention can be used to separate a liquid mixture. A liquid mixture is herein defined as a mixture of at least two compounds, whereby the at least one compound forming the continuous phase is liquid. Such mixtures include, but are not limited, to mixtures comprising two or more liquids, at least one liquid and one or more solids, at least one liquid and one or more gases. Mixtures

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comprising two or more liquids may for instance be in the form of solutions or emulsions and include molecular dispersions, micelles and droplets. Mixtures comprising at least one liquid and one or more solids may for instance be in the form of solutions of solids, suspensions or dispersions and include molecular dispersions, aggregates, and particulate dispersions. Mixtures comprising at least one liquid and one or more gases may for instance be in the form of solutions of gases, bubble dispersions or foams.

Reference herein to mixture is to be construed as including all of the above-described mixtures or any possible combination thereof, unless expressly mentioned differently.

Due to the stability of ZIFs in several environments including water and organic solvents, the process is in particular suitable for separating mixtures of hydrocarbonaceous compounds and mixtures of water and hydrocarbonaceous compounds. Such mixtures, preferably, comprise two or more compounds having a different affinity for the ZIF, the affinity of a compound for the ZIF can be for instance based on polarity, chemical nature, size, etc. By having a different affinity for the ZIF, at least the compound having the highest affinity for the ZIF will be preferentially absorbed by the ZIF. Which compound will be preferentially absorbed out of two compounds can be qualitatively measured by contacting a 1:1 mixture of the two pure compounds with a specific ZIF and subsequently determining which compound is preferentially absorbed by the ZIF using techniques known in the art, such as TDA-GC/MS (Thermal Desorption Analysis, coupled with Gas chromatography and Mass Spectrometry (GC/MS)), TDA-GC/FID (Flame Ionization

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Detector) or TDA-GC/TCD (Thermal Conductivity Detection). It will be appreciated that the chosen technique should be suitable for the compound to be analysed.

The liquid mixture may be any liquid mixture.

5 Preferably, the liquid mixture comprises water and/or one or more hydrocarbonaceous compounds. The mixtures may also comprise one or more gases. Reference herein to hydrocarbonaceous compounds is to compounds comprising at least hydrogen and carbon atoms. In addition to hydrogen
10 and carbon atoms, the hydrocarbonaceous compounds may also comprise other atoms such as for instance nitrogen, oxygen and/or halogen. Suitable hydrocarbonaceous compounds include hydrocarbons and oxygenates. Hydrocarbons are molecules consisting of carbon and
15 hydrogen atoms. Hydrocarbons may be aliphatic or aromatic. Aliphatic hydrocarbons include alkanes, alkenes and alkynes, and may be linear, branched or cyclic. Aromatics include mono aromatics, polyaromatics and substituted mono and poly aromatics, such as benzene,
20 toluene, styrene and ethylbenzene. Oxygenates are hydrocarbonaceous compounds, which comprise in addition to carbon and hydrogen atoms, one or more oxygen atoms. Examples of suitable oxygenates include alcohols, aldehydes, ketones, esters and ethers. The oxygenates may
25 be primary, secondary or branched oxygenates.

It will be appreciated that in order to effectively separate the mixture, one or more compounds in the mixture should be preferentially absorbed in the ZIF. Preferentially absorbed compounds include hydrocarbons,
30 more preferably hydrocarbons containing in the range of from 2 to 35 carbon atoms, even more preferably of from 3 to 30 carbon atoms.

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Preferentially absorbed compounds also include oxygenates, more preferably oxygenates containing in the range of from 1 to 30 carbon atoms, preferably of from 2 to 15, more preferably of from 2 to 10. Preferably, the oxygenates are branched or secondary oxygenates. It is further preferred that the oxygenates are alcohols, aldehydes, ketones, esters or ethers, more preferably alcohols.

The preferentially absorbed compound can also be a gas. The gas may be any gas such as H₂, CO, CH₄, N₂, He, Ne, Ar or Kr, however also larger gas molecules can be absorbed. The gas it will be preferentially absorbed by the ZIF, in particular when the continuous phase is water, as water is essentially excluded from the ZIF due to the hydrophobic nature of the ZIF. It is also possible to remove CO₂ from such mixtures, however it is preferred that in case of CO₂ no water is present in the mixture of is removed prior to contacting the mixture with the ZIF. When water and CO₂ are contacted simultaneously with the ZIF, the CO₂ may be irreversibly absorbed in the ZIF. In that case, the ZIF cannot be reused for further absorption steps.

Preferably, any gas to be removed does not irreversibly interact with the ZIF.

It will be appreciated that if there are more than two compounds in the mixture, it is possible that two or more compounds are absorbed by the ZIF and isolated from the original mixture.

A preferred mixture is a mixture of water and one or more hydrocarbonaceous compounds. Such mixtures may be separated as water is essentially excluded from the interior volume of the ZIF due to the polar nature of water. The maximum water uptake of a ZIF is typically in

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the order of 0.40 wt%. For comparison, known Metallic Organic Frameworks (MOF), which have structural dimensions similar to the ZIFs discussed hereinbefore have been shown to be able to absorb up to 40 wt% of water. However, silicalite zeolites, have been shown to take up as much as 50 wt% of water, as shown in M.T. Holtzapple, R.F. Brown, Conceptual design for a process to recover volatile solutes from aqueous solutions using silicalite, Sep. Technol., vol 4, 1994, p213.

10 In case the mixture comprises two or more hydrocarbonaceous compounds, independent of whether water is present in the mixture, each compound may be absorbed based on its affinity for the ZIF, whereby one compound may be preferentially absorbed over the other(s). This allows for instance to separate alcohols, such as methanol from higher alcohols. In addition, if the two or more hydrocarbonaceous compounds comprise isomers this will also allow different isomers of a hydrocarbonaceous compound to be separated, such as 1-butanol, 2-butanol and iso-butanol.

20 The process according to the invention is particularly suitable to separate dilute mixtures, preferably liquid mixtures comprising at most 50 wt% of a compound which is preferentially absorbed and which is to be isolated from the liquid mixture, based on the total weight of the mixture, more preferably in the range of from 0.0001 (1 ppm) to 50 wt%, even more preferably 0.01 to 40 wt%, still more preferably 0.1 to 20 wt%, still even more preferably in the range of from 0.5 to 6 wt%. Moreover, in case of very dilute mixtures, such as those comprising small amounts, i.e. less than 500 ppm (0.05 wt%) and preferably less than 200 ppm (0.02 wt%), of hydrocarbons or oxygenates in water, the hydrocarbon or

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oxygenate content may even be as low as 1 ppm(0.0001 wt%) to 100 ppm (0.01 wt%), preferably 5 ppm (0.0005 wt%) to 80 ppm (0.008 wt%).

5 In case there are more compounds which are preferentially absorbed and which are to be isolated, the same values apply for the combined total amount of compounds to be isolated. A method for determining the difference in affinity of two compounds for the ZIF and determining which compound is preferentially absorbed was
10 already provided herein above.

It is an advantage of the present invention that a minor component with a higher affinity to the ZIF than the major component can be isolated rather than the removing the major component, thus making it possible to
15 efficiently separate dilute mixtures.

Preferably, the mixture is contacted with the ZIF at a temperature in the range of from -200 to 500°C. The choice of the temperature depends strongly on the compounds to be separated. In case of for instance the
20 separation of higher hydrocarbons from Liquefied Natural Gas (LNG) very low temperatures in the range of from -180 to -140°C will be used. Typically, however, the mixture will be contacted with the ZIF at temperatures in the range of from 1 to 300°C, preferably from ambient
25 temperatures to 200°C.

The mixture may be contacted with the ZIF at any pressure, preferably, in the range of from 0.1 to 200 bar, more preferably of from 1 to 50 bar.

30 It is preferred that the pH of the mixture is above pH 3. Without wishing to be bound to any theory it is presently believed that some acids may react directly with the ZIF or interact with other compounds in the mixture resulting in an irreversible modification of the

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ZIF. Preferably, if an acid is present the pH of the mixture is at least 3, more preferably 3.5, or higher. Preferably, if an acid is present this is an acid comprising non or weakly co-ordinating anion(s).

5 Preferably, the mixture does not comprise an acid. Due to the stability of the ZIF in alkaline environments, the mixture may have a pH as high as 15. Preferably, the mixture has a pH of in the range of from 3.5 to 11, more preferably 5.5 to 10.

10 Following the separation process, the ZIF comprising a preferentially absorbed compound may be discarded or preferably is further processed to recover the absorbed compound and/or the ZIF. The ZIF material and/or absorbed compound may be recovered by any suitable method known in
15 the art, such as by means of a temperature treatment, sweep gas and/or vacuum, solvent extraction or elution. Suitable solvents or elution media may for instance include hydrocarbons such as pentane. Preferably, the ZIF and/or absorbed compound are recovered by heating the ZIF
20 comprising a preferentially absorbed compound to a temperature in the range of from 20 to 500°C, preferably the ZIF is heated to a temperature in the range of from 40 to 250°C. It will be appreciated that the exact choice of temperature depends on the type of ZIF and on the
25 properties of the absorbed compound. It was found that ZIF-8 releases 1-butanol when subjected to a temperature of 50°C, where typical silicalite zeolites need to be re-activated at significantly higher temperatures before a substantial release of 1-butanol is observed. Recovery
30 using a temperature treatment may take place in air, under an inert atmosphere such as nitrogen or vacuum, or in contact with a sweep gas. Subsequent to the recovery of the absorbed compound it may be preferable to re-

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activate the ZIF using a re-activation procedure, which is subject to the same boundaries as described herein above for the recovery process. The, optionally re-activated, ZIF may be reused or indeed directly recycled to the separation process, for instance in a temperature swing absorption process (TSA), wherein the liquid mixture is contacted with the ZIF at low temperature and the preferentially absorbed compound is subsequently recovered at high temperature.

10 The liquid mixture is separated by contacting the liquid mixture with the ZIF. The liquid mixture may be contacted with the ZIF by any process known in the art. This may be done in a batch process, such as for instance a TSA process as mentioned herein above, or by a
15 continues process. In a preferred way of contacting the liquid mixture with the ZIF, the liquid mixture may be mixed with the ZIF thereby forming a slurry of dispersed ZIF in a continuous phase of liquid mixture. In an
20 equally preferred alternative way of contacting, the ZIF may be provided in the form of for instance one or more packed beds or filter beds comprising the ZIF and the liquid mixture is contacted with the ZIF by flowing the liquid mixture over or through the beds.

25 The liquid mixture is contacted with the ZIF for such a period that at least part of the preferentially absorbed compound may be absorbed by the ZIF. Preferably, the liquid mixture is contacted with ZIF for a period long enough to allow at least part of the preferentially absorbed compound to be absorbed but no longer than the
30 time necessary to reach the equilibrium concentration of preferentially absorbed compound. Reference herein to the equilibrium concentration is to the concentration of preferentially absorbed compound in the liquid mixture at

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which no further decrease of the concentration of preferentially absorbed compound in the liquid mixture is observed in time.

5 The ZIF may be contacted with the mixture in any form or shape. Typically, the ZIF is in the form of particles. The particles can have any form suitable for the planned use. Preferably, the particles are pellet, tablet or bar shaped. In the context of the present invention, the term particle preferably refers to any
10 solid body that extends to at least 0,2 mm in at least one direction in space. No other restrictions apply, i.e., the body may take any conceivable shape and may extend in any direction by any length so long as it preferably extends to at least 0.2 mm in one direction.
15 In a more preferred embodiment, the shaped bodies do not extend to more than 50 mm and not to less than 0,2 mm in all directions. In a further preferred embodiment, the shaped bodies do not extend to more than 1 mm and not to less than 16 mm in all directions, preferably not extend
20 to more than 1,5 mm and not to less than 5 mm. Optionally, the ZIF particles may comprise a binder material. Alternatively, the ZIF may also be supported, e.g. on known supports like metal or inorganic supports or in pouches.

25 The ZIF may also be comprised in a membrane. The membrane may essentially consist of ZIF, however it is preferred that the membrane is a composite membrane comprising a layer of ZIF supported by a polymeric, inorganic or metal support. Alternatively, the ZIF is
30 dispersed in an inorganic or polymeric membrane material. The ZIF material may for instance be incorporated in a silica membrane using a silica solution comprising both the ZIF as well as silica. Preferably, the ZIF is

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dispersed in a polymeric membrane material, such as a silicon rubber (PDMS), polyimide, polyamide, polyaramide, polysulphone, polyethersulphone, polyvinyl alcohol or cellulose acetate type polymer. Preferably, a rubbery polymer is used to enhance interaction between the ZIF and the polymer matrix by reducing the formation of voids at the ZIF/polymer interface. In case of aqueous mixtures it is preferred to use a hydrophobic polymer material, more preferably a rubbery hydrophobic material such as PDMS. The ZIF may be incorporated in any form or structure, such as a particle or a crystal. Preferably, the ZIF structure has an average diameter of no more than the thickness of the polymeric membrane layer, typically the membrane thickness is about 500 nm. More preferably, no more than half of the thickness of the polymeric membrane layer. Even more preferably, in the range of from 1 to 100 nm.

Such a membrane may be used in known membrane separation processes, such as micro filtration, ultrafiltration, reverse osmosis, nanofiltration and pervaporation. It will be appreciated that when choosing a polymeric membrane material, the stability of such a polymeric membrane material is taken into consideration in the presence of either water or any hydrocarbonaceous compound in the mixture is considered.

The ZIF may be any suitable ZIF, preferably the ZIF is ZIF-1, ZIF-2, ZIF-3, ZIF-4, ZIF-5, ZIF-6, ZIF-7, ZIF-8, ZIF-9, ZIF-10, ZIF-11, ZIF-12, ZIF 14, ZIF-20, ZIF-21, ZIF-22, ZIF-23, ZIF-60, ZIF-61, ZIF 62, ZIF-63, ZIF-64, ZIF-65, ZIF-66, ZIF-67, ZIF-68, ZIF-69, ZIF-70, ZIF-71, ZIF-72, ZIF-73, ZIF-74, ZIF-75, ZIF-76, or a mixture of one or more thereof. More preferably, the ZIF is ZIF-8, ZIF-10, ZIF-11, ZIF-12, ZIF-20, ZIF-21, ZIF-65,

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ZIF-67, ZIF-68, ZIF-70, ZIF-71, ZIF-76 or a mixture of one or more thereof. These preferred ZIFs combine a good thermal and chemical resistance properties with a large internal volume, i.e. the framework will accommodate a sphere having a diameter of over 10 Angstrom. Even more preferably, ZIF-8 (Zn,2-methyl-imidazole), as this is commercially available. It will be appreciated that the internal volume of a ZIF may affect its separation properties. For instance a large internal volume allows for a high absorption capacity, whereas using a ZIF with a lower internal volume may result in an even higher selectivity.

The process according to the present invention is particularly, but not exclusively, suitable for separation of the following mixtures:

Dilute aqueous mixtures comprising one or more alcohols. Examples of such mixtures include aqueous fermentation broths obtained in fermentation processes or organic materials for the production of bio-alcohols such as bio-ethanol and bio-butanol for biofuel purposes. Such aqueous fermentation broths typically comprise up to 18 vol% of alcohol, based on the volume of the alcohol/water mixture. Of particular interest is the separation of mixtures of water and butanol (1-butanol, 2-butanol and/or iso-butanol). 1-butanol, 2-butanol and iso-butanol are suitable for biofuel applications due to their high energy content and simple production process, i.e. fermentation. However, the low butanol tolerance of the bacteria used in this process leads to dilute aqueous solutions (1-2w%) and high energy consumption during recovery. The process according to the present invention allows for the efficient removal of butanol from such very dilute mixtures. In accordance, the present

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invention also provides a process for the separation of alcohols from aqueous fermentation broths.

Effluent streams comprising dilute amounts of MTBE may also be efficiently separated to remove MTBE. In accordance, the present invention also provides a process for the separation of MTBE from MTBE-comprising streams.

Dilute aqueous mixtures comprising oxygenates and/or hydrocarbons for instance are obtained as process water from a Fischer Tropsch reaction for the synthesis of hydrocarbons from synthesis gas. In a Fischer-Tropsch reaction, water is produced as a by-product together with the desired hydrocarbons. In addition, some lower oxygenates, such as C1 to C5 alcohols, aldehydes and ketones are formed. The produced water may contain those oxygenates and additionally some hydrocarbons, which must be removed from the produced water for environmental reasons. This can be done using the process according to the present invention. In accordance, the present invention also provides a process for the separation of oxygenates and/or hydrocarbons from process water from a Fischer Tropsch reaction or any aqueous effluent from a Gas-to-Liquids process.

Very dilute mixtures comprising water and hydrocarbons, especially mixtures comprising less than 200 ppm, preferably less than 100 ppm more preferably less than 50 ppm of hydrocarbons. Hydrocarbons found in these mixtures include paraffins, olefins and aromatics. Such very dilute aqueous mixtures are commonly obtained in oil related processes. Examples thereof include the aqueous effluent streams of oil and gas production platforms. Oil refineries produce many aqueous effluent streams such as the effluent of the desalter unit. Of particular interest are the settling ponds for aqueous

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effluents of heavy bitumen upgrading processes, e.g. oils
tar sands and oil shales. Also aqueous mixtures obtained
during the clean-up of hydrocarbon spills, such as on
refinery sites and petrol supply stations. Often, the
5 aqueous mixtures are brines comprising 10 to 95 mol% of
salt, based on the weight of the total mixture.

These dilute aqueous mixtures are typically
collected in settling ponds, tanks or other types of
settlers wherein the mixture is allowed to separate into
10 an upper hydrocarbonaceous layer on top of an aqueous
bulk. This hydrocarbonaceous layer typically comprises
hydrocarbons containing in the range of from 10 to 30
carbon atoms. Smaller hydrocarbons, preferably containing
in the range of from 3 to 15 carbon atoms, may be present
15 in the aqueous bulk as dissolved species or in the form
of micelles or emulsions. These dilute aqueous mixtures
typically have a pH in the range of from 3.5 to 9.

At concentrations above 3 wt% of hydrocarbonaceous
compounds, the hydrocarbonaceous compounds are typically
20 removed by skimming the upper layer from the aqueous
bulk. However, below 3 wt% it is nearly impossible to
efficiently remove such small amount using conventional
processes. A known method is the use of active coal
absorbents. However, this results in significant amounts
25 of spent active coal, which needs to be disposed.

In one aspect, the process according to the present
invention utilises a ZIF for separating the hydrocarbons
from the aqueous bulk of the mixture. ZIF have high
surface areas, several fold, approximately 2 to 5 times,
30 higher compared to active coal, and can therefore absorb
significantly more hydrocarbons per unit volume. This
allows for an efficient removal of the hydrocarbons.
Contrary to the active coal, the ZIF can be regenerated

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and reused and need not be disposed of. Moreover, even if the ZIF would be disposed of the waste volumes are significantly smaller due to the high absorption per unit volume, thereby reducing the size of the waste problem significantly. In accordance, the present invention also provides a process for the separation of hydrocarbons from the aqueous effluent streams of oil and gas production platforms or refinery units. In accordance, the present invention also provides a process for the separation of hydrocarbons from the aqueous effluents of heavy bitumen upgrading processes. In particular from the settling ponds, wherein aqueous effluents of heavy bitumen upgrading processes remain.

Mixtures of methanol and higher alcohols, such as ethanol, propanol, butanol and pentanol can also be separated using the process according to the invention. Such mixtures may for instance be obtained as the effluent of a syngas-to-alcohol process. In accordance, the invention also provides a process for separating mixtures of alcohols.

Mixtures of normal and branched alkanes or primary, secondary or branched alcohols can also suitably be separated using the process according to the invention. Such separation may be of particular use in the field of biofuels, e.g. separation of 1-butanol, 2-butanol and iso-butanol, and in the field of hydrocarbon fuels, i.e. the separation of normal and iso paraffins.

Mixtures of ethylbenzene and styrene are obtained from for instance a Styrene Monomer/Polyethylene oxide (SM/PO) process. Presently, this mixture is separated by distillation, however it is now also possible to separate this mixture using the process according to the invention. In accordance, the invention also provides a

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process for separating mixtures of ethylbenzene and styrene, which are obtained from a Styrene Monomer/Polyethylene oxide (SM/PO) process

5 Due to the stability of the ZIFs in alkaline environments the process according to the present invention is particularly suitable for separating alkaline mixtures such as those obtained from a saponification process where typically a strong base, such a NaOH, is used as a catalyst.

10 The invention is further illustrated by the following non-limiting examples:

Example 1: Separation of diluted aqueous alcohol solutions.

15 ZIF-8 (BASOLITE Z1200 ex Aldrich) was evacuated (< 1 mbar) at 200°C for 16-20 hours prior to contacting it with the aqueous alcohol solution.

Diluted aqueous alcohol solutions were prepared by mixing the alcohol with demineralised water.

20 In each experiment the evacuated ZIF-8 was immersed in the diluted aqueous alcohol solution for 24 hours at ambient temperature.

Subsequently, the solution together with the ZIF-8 was filtrated over a P4 glass filter. The liquid filtrate was collected.

25 Both the filtrate and the original aqueous alcohol solution were analyzed with GC/FID. The quantity of alcohol absorbed by the ZIF was calculated from the reduction of the alcohol GC peak area.

Table 1

Example	Alcohol	ZIF-8	Aqueous alcohol solution	Initial alcohol concentration	Final alcohol concentration	% of alcohol removed
		[gram]	[gram]	[wt%] *	[wt%] *	[%] **
1A	methanol	0.73	10.00	5.21	5.06	2.8
1B	ethanol	0.30	4.45	4.19	3.23	22.9
1C	1-propanol	0.73	11.94	5.00	3.21	35.8
1D	2-propanol	0.73	12.33	5.08	3.40	33.1
1E	1-butanol	0.21	2.80	3.02	0.73	75.9
1F	2-butanol	0.77	10.83	5.25	3.17	39.6
1G	Iso-butanol	0.74	11.20	4.93	3.02	38.7
1H	1-pentanol	0.413	9.11	0.32	<0.01	97.2
1I	1-octanol	0.41	10.60	0.044	<0.0001	99.9

* based on the weight of the total solution

** based on the initial concentration

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Table 1 gives an overview of the prepared aqueous solutions and the obtained reduction of the alcohol concentration. It will be clear that all tested alcohols can be selectively removed from the aqueous solution. The best results were obtained with alcohols comprising 2 to more carbon atoms. More than 90 wt% of C5+ alcohols were removed from the solution by contact with the ZIF

Example 2: Recovery of 1-butanol from ZIF-8

The filter residue obtained in Example 1E was dried by evacuation at ambient temperature for 10 minutes and subsequently analyzed with TDA-GC/MS (thermal Desorption Analysis, coupled with GC/MS).

This revealed that all (>99 wt%) of the absorbed matter, i.e. 1-butanol and water, can be removed at 50°C and that its purity is >99%. 1-butanol of such purity may for instance be used directly for biofuel application. Further TDA-GC/MS analysis at temperatures above 100°C did not detect additional matter being desorbed.

From this experiment it can be concluded that 1-butanol is selectively absorbed over water with a selectivity over 100, whereby the selectivity is defined as the ratio of the absorbed amount (wt%) of 1-butanol over the absorbed amount (wt%) of water. Similar experiments were performed using a zeolite ZSM-5 absorbent. These experiments showed a 1-butanol over water selectivity of less than 0.5, approximately 0.1 grams of 1-butanol and 0.3 grams of water were absorbed per gram of zeolite. This is comparable to M.T.Holtzapple, R.F. Brown, Conceptual design for a process to recover volatile solutes from aqueous solutions using silicalite, Sep. Technol., vol 4, 1994, p213, where an 1-butanol over water selectivity of 1 is reported.

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Example 3: Absorption of alcohol by ZIF-8.

From the results obtained in Example 1, the amount of alcohol absorbed per amount of ZIF-8 was determined in order to give an indication of the absorption capacity of ZIF-8. The results are shown in Table 2. It will be clear that ZIF-8 can selectively absorb high weight percentages of alcohols. It should be noted that it was not the aim to determine the maximum absorption capacity for each alcohol. For example, it is expected that in case of experiments 1H and 1I, i.e. 1-pentanol and 1-octanol, the maximum absorption capacity is significantly higher than the absorption reported in Table 2 as very dilute solution were used. Similar absorption experiments using a zeolite ZSM-5 absorbent, showed a maximum 1-butanol absorption, which was almost 3 times lower than the absorption found for ZIF-8.

Table 2.

Example	Alcohol	Wt% alcohol in ZIF
		[wt%] *
1A	methanol	2.0
1B	ethanol	14.0
1C	1-propanol	29.0
1D	2-propanol	28.0
1E	1-butanol	29.2
1F	2-butanol	29.0
1G	Iso-butanol	29.0
1H	1-pentanol	6.9
1I	1-octanol	1.0

* based on the dry weight of the ZIF

Due to the different affinity of the ZIF for different alcohols, it is also possible to separate mixtures of alcohols. Therefore, the present invention also relates to the separation of mixtures comprising more than one alcohol, in particular the separation of mixtures comprising methanol and one or more higher alcohols.

Example 4: Separation of diluted solutions

In Experiment 1, a relatively high concentration of alcohol was used. To determine the effect of concentration on the separation ability of the ZIF several solutions were prepared of 1-butanol in demineralised water. Pre-treated ZIF-8 was immersed in the prepared solution in a quantity such that the equilibrium concentration was lowered from 3.6 to approximately 0.5. Table 3 shows the wt% of 1-butanol in ZIF-8 at each equilibrium concentration.

Table 3

Initial alcohol concentration	Equilibrium alcohol concentration	Wt% alcohol in ZIF at equilibrium
[wt%] *	[wt%] *	[wt%] *
7.1**	3.6	31.0
3.0	1.7	29.9
3.0	0.7	30.2
3.0	0.6	30.0

* based on the dry weight of the ZIF

** saturated

It can be concluded that saturation concentration of 1-butanol in ZIF-8 was already reached at a equilibrium concentration of 0.6%, as the amount of 1-butanol absorbed did not further significantly increase at higher equilibrium concentrations. The amount of 1-butanol absorbed is approximately 30%wt. Thus, ZIF-8 is able to absorb 0.3 gram of 1-butanol per gram of dry product at 1-butanol levels in water of 0.6 wt% and above. This is about three times as much as achieved with typical silicalites known in the art. It will be appreciated that the ability of the process according to the invention to separate very dilute mixtures was already shown in Examples 1H and 1I, and is shown again in Example 5, herein below.

Example 5a: Separation of diluted aqueous hydrocarbon solutions.

Following the same procedure as in Example 1, a saturated aqueous solution of toluene was separated.

The results are shown in Table 4.

Table 4

hydrocarbon	ZIF-8	Aqueous hydrocarbon solution	Initial hydrocarbon concentration	% of hydrocarbon removed
	[gram]	[gram]	[wt%] *	[%] **
Toluene	0.40	9.23	Saturated, ~500 ppm	> 99 [#]

* based on the weight of the total solution

** based on the initial concentration

no toluene peak observed in GC-analysis

Example 5b: Separation of diluted aqueous hydrocarbon solutions.

An aqueous solution of benzene was continuously passed through a bed of ZIF-8 pellets. The benzene content in the effluent was measured to determine the break-through concentration.

ZIF-8 (BASOLITE Z1200 ex Aldrich) was evacuated (< 1 mbar) at 200°C for 16-20 hours. ZIF-8 was pelletized under a pressure of 3 ton, to produce ZIF-8 pellets. The pellets were subsequently crushed and sieved to obtain ZIF-8 particles having a particle size in the range of from 212 to 500 µm. 2.2 grams of the thus prepared ZIF-8 particles were used to form an adsorption bed having an approximate volume of 6.1 ml.

An aqueous benzene solution comprising 351.5 mg benzene per litre was prepared by mixing benzene with demineralised water. The solution was passed upwards through the adsorption bed with a flow rate of 1.6 ml per hour at ambient temperatures and pressures. The benzene concentration in the effluent was analyzed at several time intervals using GC/FID. The quantity of benzene

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absorbed by the ZIF was calculated from the reduction of the benzene GC peak area.

5 The results are shown in Table 5. It will be clear that the removal of benzene from the aqueous benzene solution is almost complete until breakthrough occurs beyond a total benzene loading of approximately 20g benzene/100g ZIF-8.

Table 5.

Sample	Benzene solution added (cumulative)	Benzene added (cumulative)	Benzene conc. in effluent
	[ml]	[mg]	[mg/l]
1	0.0	0.0	> 0.05*
2	7.0	2.5	> 0.05*
3	191.0	67.1	> 0.05*
4	360.6	126.7	0.44
5	536.6	188.6	1.66
6	712.6	250.5	5.48
7	1156.0	406.3	3.51
8	1328.8	467.0	39.98
9	1503.2	528.3	47.65

* Below the detection limit of 0.05 ppm

Example 6: Regeneration of ZIF

10 A ZIF-8 sample was pre-treated as described under Example 1. A methane sorption isotherm was recorded at 20°C in the pressure range of 0 to 55 bar. Subsequently, the ZIF-8 was immersed in a solution of ethanol in demineralised water (the same as was used in example 1B) following the procedure of Example 1. Following the
15 ethanol absorption the ZIF-8 sample was evacuated at a temperature of 200°C to remove the ethanol and again the

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methane sorption isotherm was recorded at 20°C in the pressure range of 0 to 55 bar. No loss of absorption volume was observed.

Example 7: ZIF stability in acid environment.

5 Solutions of HCl in demineralised water were prepared. A sample of ZIF-8 was pre-treated as described in Example 1 and subsequently immersed in the HCl solutions. It was found that ZIF-8 was structurally unstable in a 1 M (mole/l, pH 0) solution of HCl.
10 However, the ZIF-8 remained stable in a solution of 0.001 M HCl (pH 3).

Example 8: Water adsorption.

 The water adsorption of several materials was tested. Prior to the exposure to water all materials were
15 pre-treated in a nitrogen atmosphere for 90 min at 150°C.

 Water adsorption was determined using continuous adsorption/desorption process. Adsorption was measured by contacting the sample material under atmospheric pressure with a nitrogen stream comprising water vapour at a water
20 partial pressure of 2000Pa for a time period of 90 minutes. The temperature during adsorption was maintained at 30°C. Regeneration took place at a temperature of 100°C for a time period of 90 minutes under a nitrogen atmosphere at atmospheric pressure. The adsorption
25 desorption cycle was repeated 100 times. Water uptake was determined using Thermal Gravimetical Analysis (TGA), the TGA results were corrected for buoyancy differences.

 The following materials were tested: MOF-5, MOF-177, Cu-BTC, Fe(III)-BTC, MIL-53, and ZIF-8. The results are
30 reported in Table 6. It will be clear that the ZIF material in particular ZIF-8, show an exceptionally low water uptake. It was further observed that MOF-5, MOF-177 and CU-BTC were not stable in water. It was found that

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not all water could be desorbed and part of the water was irreversibly adsorbed. A separate experiment determining the water uptake of a ZSM 5 zeolite adsorbent, based on the absorption of water from an 1% 1-butanol in water solution using TGA-MS as analysis method, showed a maximum water uptake as high as 50 wt%.

Table 6.

Sample	Water uptake
	[wt%]
ZIF-8 ¹	<0.4 ³
MOF-5 (Zn-BDC) ²	14 ⁴
MOF-177 (Zn-BTB) ²	8 ⁴
Cu-BTC ¹	47 ⁴
Fe(II)-BTC ¹	23
MIL-53 ¹ (Al-BDC)	4

BDC: Benzene-1, 4-dicarboxylic acid or terephthalic acid

BTC: Benzene-1, 3, 5-tricarboxylic acid or trimesic acid

BTB: Benzene 1,3,5-tribenzoate

1: ex Sigma Aldrich

2: prepared in-house

3: below detection limit

4: adsorption partially irreversible

C L A I M S

1. A process for the separation of a liquid mixture using a ZIF.
2. A process according to claim 1, wherein the liquid mixture comprises two or more compounds having a
5 different affinity for the ZIF.
3. A process according to claim 1 or 2, wherein the liquid mixture comprises water and/or one or more hydrocarbonaceous compounds.
4. A process according to any one of the preceding
10 claims, wherein the liquid mixture comprises one or more gases.
5. A process according to any one of the preceding claims, wherein the liquid mixture is an aqueous mixture comprising water and one or more hydrocarbonaceous
15 compounds.
6. A process according to any one of the preceding claims, wherein the liquid mixture comprises at least one hydrocarbonaceous compound and the hydrocarbonaceous compound is a hydrocarbon or an oxygenate, preferably a
20 hydrocarbon or an alcohol.
7. A process according to any one of the preceding claims, wherein the mixture comprises two or more hydrocarbonaceous compounds.
8. A process according to claim 7, wherein the two or
25 more hydrocarbonaceous compounds comprise isomers.
9. A process according to claim 7 or 8, wherein the hydrocarbonaceous compounds are oxygenates, preferably alcohols.
10. A process according to any one of the preceding
30 claims wherein the ZIF is one of ZIF-8, ZIF-10, ZIF-11,

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ZIF-12, ZIF-20, ZIF-21, ZIF-65, ZIF-67, ZIF-68, ZIF-70, ZIF-71, ZIF-76 or a mixture of one or more thereof, more preferably ZIF-8.

5 11. Process according to any one of the preceding claims, wherein the liquid mixture comprises at most 50 wt% of a preferentially absorbed compound, preferably in the range of from 0.01 to 40 wt%, more preferably of from 0.1 to 20 wt% based on the total weight of the mixture.

10 12. Process according to any one of claims 1 to 10, wherein the liquid mixture comprises at most 500 ppm of a preferentially absorbed compound, preferably in the range of from 1 ppm to 100 ppm, more preferably of from 5 to 80 ppm.

15 13. A process according to any one of the preceding claims, wherein the liquid mixture has a pH in the range of from 3 to 15, preferably 3.5 to 11.

20 14. Process according to any one of the preceding claims, comprising contacting the liquid mixture with the ZIF by mixing the liquid mixture with the ZIF thereby forming a slurry.

15. Process according to any one of the preceding claims, comprising contacting the liquid mixture with a fixed bed comprising the ZIF.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/059555

A. CLASSIFICATION OF SUBJECT MATTER
 INV. B01D17/02 B01D17/08 B01D19/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/054581 A2 (BASF AG [DE]; MUELLER ULRICH [DE]; HESSE MICHAEL [DE]; SCHUBERT MARKUS) 18 May 2007 (2007-05-18) abstract; examples page 5, line 31 - line 32 page 6, lines 11,13,18 page 28, lines 1,4,5,9,15 -----	1-15
X	EP 1 702 925 A1 (BASF AG [DE]) 20 September 2006 (2006-09-20) abstract; examples page 4, lines 16,27,33 -----	1-15
A	WO 84/04913 A (ZEOL AB [SE]) 20 December 1984 (1984-12-20) abstract; figures; example 1 page 2, line 25 - line 28 ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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